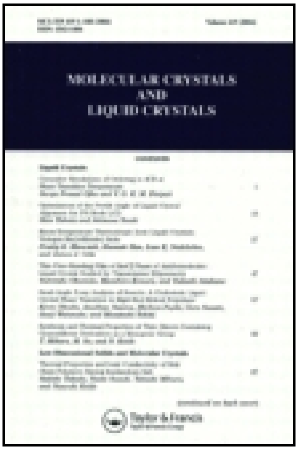

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Photochromic Polymers Based on Methacrylic Azoesters

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Photochromic Polymers Based on Methacrylic Azoesters

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The new polymers and copolymers based on methacrylic acid azoesters with substituents of different nature and spacer length were synthesized. The difference in chemical structure of the side chains was expected to influence on the difference in the supramolecular structure of azobenzene moieties. Due to flexibility of alkyl spacers, the azobenzene fragments can rotate relatively freely in the polymeric matrix.

Keywords: absorption spectra; azopolymers; phase transition

1. INTRODUCTION

Polymers containing linked photochromic moieties such as azobenzene derivatives are known as azopolymers. These materials exhibit photoinduced optical anisotropy of extremely high efficiency [1], that makes azopolymers particulary suitable for the investigation of light-induced ordering processes. That is why in the last decade these polymers have been the subject of the intensive experimental and theoretical studies [2–6].

The optical response of the polymer is mainly influenced by three structural factors: the polymer backbone, the structure of the azo chromophore and the linkage between the backbone and the azochromophore. The type of polymer backbone mostly dictates the mechanical properties, such as the glass temperature (T_g) of the polymer. The linkage between the azo chromophore and the polymer backbone affects both the mechanical properties and the motion of the azo

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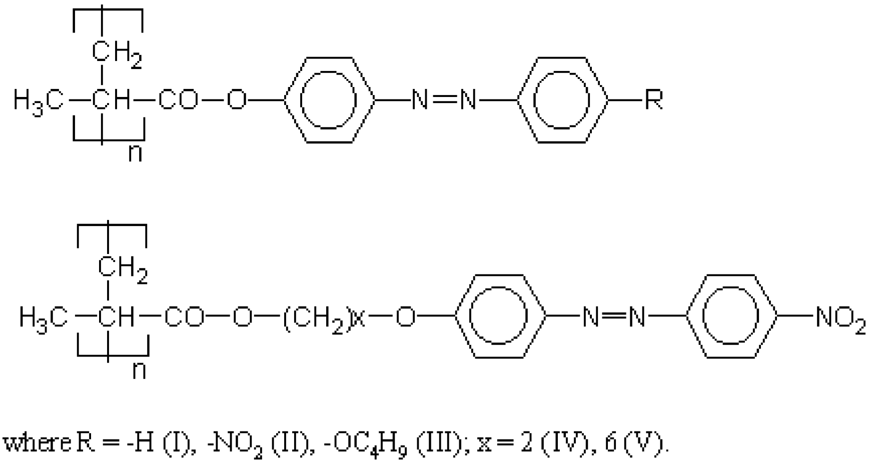


where R = -H (I), $-NO_2$ (II), $-OC_4H_9$ (III); x = 2 (IV), 6 (V).

SCHEME 1 Photochromic azopolymers.

groups, and thus their orientation. The structure of the azo chromophore determines properties such as the wavelength of maximum absorbance, the cis-trans thermal isomerization rate, the orientation ability, as well as the order parameter.

We report here the synthesis and investigation of the photochromic polymers and copolymers based on methacrylic such azoesters (Scheme 1):

The side chains of obtained polymers contain flexible alkyl spacers of different length and groups of the different nature. The difference in chemical structure of the side chains was expected to influence on the difference in the supramolecular structure of azobenzene moieties. Due to flexibility of alkyl spacers, the azobenzene fragments can rotate relatively freely in the polymeric matrix.

2. EXPERIMENT

The corresponding monomers was synthesized by general methods. Azocompound (0.06 mol) and triethylamine (9.0 mL) were dissolved in THF (200 mL). The solution was kept in an ice bath for 10 min. A solution of distilled methacryloyl chloride (6.0 mL, 0.06 mol) was added slowly to the above mixture. After the addition of methacryloyl chloride, the resulting mixture was stirred at room temperature overnight. Then the solution was poured into distilled water (1 L) and the obtained residue was filtered and air dried. Recrystallization of monomers was carried out from the ethanol.

Methyl methacrylate was purified by distillation before use.

Copolymers as well as homopolymers were synthesized by free-radical polymerization in toluene. Toluene was dried by refluxing over sodium.

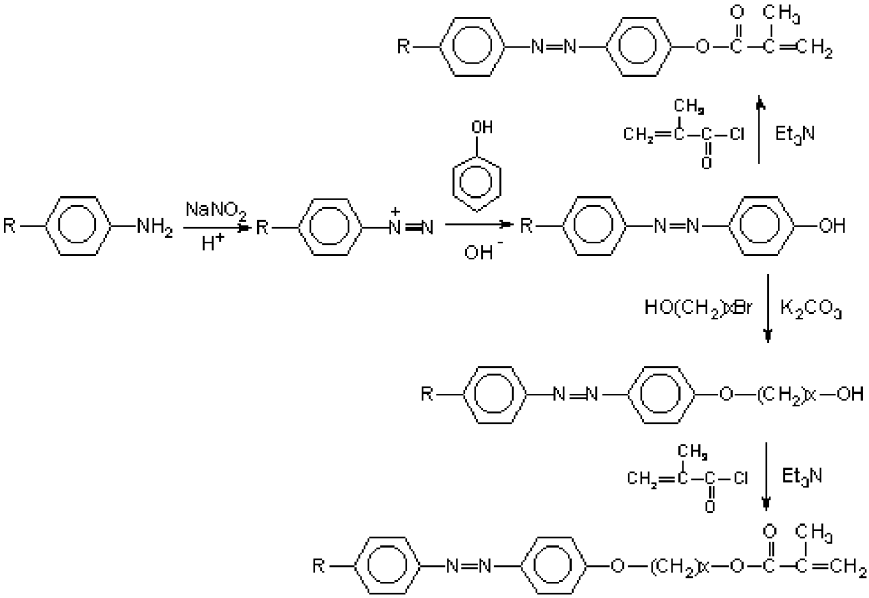
The polymerization was carried out in 10% toluene solution containing AIBN free radical initiator 10% of the monomers by weight at 80°C more than 30 hours. Polymers were isolated from the reaction by precipitation into methanol followed by reprecipitation from toluene into methanol and then dried at 20°C overnight.

^{1}H-NMR-spectra were obtained on a Varian Mercury-400 spectrometer. Thermal transition were measured on a Perkin Elmer DSC-2 instrument equiped with a IFA GmbH processor at the scan rate of 20°K/min.

3. RESULTS AND DISCUSSION

Scheme 2 gives the synthesis route for the corresponding azomonomers.

The synthesized monomers were characterized by elemental analysis and ^{1}H NMR spectroscopy. The results are in a good agreement with the proposed structures. All synthesized compounds are able to copolymerization with methyl methacrylate and styrene. It was found



SCHEME 2 The synthesis route for the monomers.

TABLE 1 The Phase Transition and Absorption Maximum for Azopolymers

Polymer	Phase transition,°K	Maximum of absorbance, nm
I	392.6	345–348
II	433.5	350–354
III	430.2	348–350
IV	386.1	355–358
V	384.8	362–365

that polymerization of corresponding azomonomers needs a long time, and the best polymer yields were obtained, when more then 10% (weight) of initiator were added. Synthesized polymers and copolymers are solids at room temperature and dissolved in benzene, toluene, dichloroethane, dioxane. The phase transition and absorption maximum for azopolymers I, II, III, IV and V are presented in Table 1.

We can conclude that presence of substituents in p-position to azo-group leads to the increase of polymer T_g due to more rigid structures formation. In parallel, spacer incorporation in a side fragment leads to the decrease of the polymer T_g due to chomophores flexibility appearance what also causes batochromic shift of homopolymer absorbance maximum.

Spectral investigations show that obtained polymers have photochromic properties and can be proposed as materials for nonlinear optics.

CONCLUSIONS

Polymers containing substituted azobenzene groups were synthesized. Temperature characteristics and absorption spectra of synthesized polymers were investigated.

Obtained polymers may be suggested as materials for optical data storage, holography and photo-switching of optical elements.

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